

APPLICATION
FOR
UNITED STATES LETTERS PATENT

10 Be it known that we, John R. Williams, residing at 70 Outlook Drive, Lexington,
Massachusetts 02421; and Brian T. Cunningham, residing at 23 Bedford Street, Lexington,
Massachusetts 02420, and being citizens of the United States, have invented a certain new
and useful

15 APPARATUS AND METHOD FOR MEASURING
THE MASS OF A SUBSTANCE

of which the following is a specification:

EL507340515US)

Applicant: Williams et al.
For: Apparatus and Method for Measuring the Mass of a Substance

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FIELD OF INVENTION

This invention relates generally to an apparatus and method for measuring the mass of a substance, and more particularly to an apparatus and method for monitoring the reference resonant frequency of a flexural plate wave sensor, determining the change in frequency after the substance is placed on the sensor and the determining the mass of the substance based on the change in the reference resonant frequency.

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BACKGROUND OF INVENTION

Prior art mass measuring devices, such as microbalances, are capable of measuring substances within the microgram range. However, in some circumstances, it is necessary to 15 measure the mass of a substance or the change in the mass of a substance which is in the nanogram or subnanogram range. Such circumstances include the determination of the moisture content of a substance, the boiling point of a substance and the determination of a concentration of non-volatile residues (NVR) in solvents.

One prior art method for determining the concentration of a NVR in a solvent 20 involves boiling a large quantity of a solvent sample, typically a liter or more, in a glass container until the entire sample is evaporated. Any material remaining after the boiling process is non-volatile residue. A microbalance is then used to measure the weight of the material remaining after boiling. However, this process has many disadvantages. First, a large quantity of solvent must be boiled away in order to provide enough mass gain to be

resolved by the microbalance; boiling and measuring operation can take several hours; and the boiled solvent is exhausted into the atmosphere. The procedure is labor intensive and reproducibility problems are present due to the ease of contamination during long exposure time of the sample to the atmosphere during the boiling process.

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SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method and apparatus for determining the mass of a substance.

It is a further object of the invention to provide such an apparatus and method that is capable of determining the mass of a substance with a resolution in the nanogram or 10 subnanogram range.

It is further object of the invention to provide such a method and apparatus that is capable of determining the mass of a substance in a quick and simple manner.

It is a further object of the invention to provide such as apparatus and method that monitors the change in the reference resonant frequency of a flexural plate wave sensor to 15 determine the mass of a substance disposed on the sensor.

It is a further object of the invention to provide such a method and apparatus for determining the concentration of the substance in a solution, based on the determination of the mass of the substance.

It is a further object of the invention to provide such a method and apparatus for 20 determining the moisture content of the substance based on the determination of the mass of the substance.

It is yet a further object of the invention to provide such a method and apparatus for determining the boiling point of the substance based on the reduction in the mass of the

substance as the substance is heated.

The invention results from the realization that a truly effective mass determining device can be obtained by driving the membrane of a flexural plate wave sensor at a reference resonant frequency, placing a substance on the membrane of the flexural plate

5 wave sensor, determining the frequency change in the membrane as the result of the deposition of the substance on the membrane and determining the mass of the substance based on the change in the frequency within the membrane. The concentration of a substance within a solution can be determined by comparing the mass of the substance, which is determined based on the frequency change within the membrane, to the volume of

10 the solution in which the substance is located. The moisture content of the substance also can be determined by determining the mass of the substance based on the frequency change within the membrane, heating the substance to evaporate moisture contained within the substance and determining the mass of the substance after the moisture is driven off, wherein the change in the mass of the substance is a result of the heating process is

15 indicative of the moisture content of the substance. Furthermore, the boiling point of a substance also can be determined based on the rate of the change of the mass of the substance as it is heated.

This invention features an apparatus for measuring the mass of a substance including a sensor having a membrane layer, the membrane for receiving the substance thereon, an oscillator device for driving the membrane at a reference resonant frequency, a frequency detection device for determining a change in the reference resonant frequency caused by the presence of the substance on the membrane and a mass determining device for determining the mass of the substance, the change in the reference resonant frequency

being indicative of the mass of the substance.

In a preferred embodiment, the sensor maybe a flexural plate wave sensor. The flexural plate wave sensor may be formed from a silicon substrate and the membrane may be formed from a silicon layer. The flexural plate wave sensor may further include a piezoelectric layer formed on the membrane, a first transducer disposed on the piezoelectric layer and a second transducer disposed on the piezoelectric layer, spaced from the first transducer. The oscillator device may be connected to the first transducer for driving the membrane at the reference frequency and the frequency detection device may be connected to the second transducer for determining the change in the reference resonant frequency. The sensor may further include a plurality of walls peripheral to the membrane, the plurality of walls cooperating to define a cavity having the membrane as a bottom portion thereof. The deposition of the substance on the membrane may cause a decrease in the reference resonant frequency, thereby indicating an increase in the mass disposed on the membrane. An increase in the reference resonant frequency may indicate a decrease in the mass of the substance on the membrane. The substance may be present in a volume of a volatile solution which is deposited on the membrane, the mass of the substance being measured after the solution evaporates, leaving the substance on the membrane. The apparatus may further include a concentration determining device for comparing the mass of the substance to the volume of the solution to determine the concentration of the substance within the volume of the solution. The substance may be a non-volatile residue. The apparatus may further include a display device connected to the microprocessor for displaying the mass of the substance. The apparatus may further include a heating device for heating the substance after it has been deposited on the

membrane to evaporate moisture from the substance, the frequency detection device determining the change in the reference frequency after the moisture is evaporated from the substance. The apparatus may further include a moisture content determining device, wherein the mass determining device determines the mass of the substance after the

5 substance is heated and the moisture content determining device determines the moisture content of the substance by comparing the mass of the substance before it is heated to the mass of the substance after it is heated. The apparatus may further include a boiling point determining device, wherein the heating device may heat the substance with a temperature which is increasing at a constant rate which causes the reference resonant

10 frequency to increase at a first rate as the mass of the substance decreases, the frequency detection device may monitor the rate of change of the reference resonant frequency as the substance is heated and the boiling point determining device may determine the boiling point of the substance as the temperature when the rate of change of the reference frequency becomes greater than the first rate. The apparatus may include a plurality of

15 sensors configured in an array, each of the sensors being connected between the oscillator device and the frequency detection device.

The invention also features a method for measuring the mass of a substance, including the steps of driving a membrane of a sensor at a reference resonant frequency, depositing the substance onto the membrane of the sensor, measuring a shifted frequency within the membrane, detecting a change of the shifted frequency from the reference frequency, and determining the mass of the substance based on the change of the shifted frequency from the reference resonant frequency.

In a preferred embodiment, the depositing step may include placing a volume of

volatile solution containing the substance on the membrane and allowing the solution to evaporate, the substance thereby remaining on the membrane. The method may further include the step of comparing the mass of the substance to the volume of the solution to obtain the concentration of the substance within the solution. The method may further

5 may further include the steps of heating the substance after the mass of the substance is determined to drive out any moisture in the substance, measuring the post-heating frequency in the membrane after the heating step, detecting a change of the post-heating frequency from the shifted frequency, and determining the mass of the substance after the heating step based on the change of the post heating frequency from the shifted

10 frequency. The method may further include the step of determining the moisture content of the substance before the heating step takes place, based on the difference in the mass of the substance before the heating step and the mass of the substance after the heating step. The depositing step may include placing the sensor in a fluid environment and allowing a volatile solution contained in the fluid environment to collect on the

15 membrane.

The invention also features an apparatus for measuring a change in the mass of a substance within the subnanogram range.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings, in which:

 Fig. 1 is a block diagram of the mass determining apparatus in accordance with the present invention;

Fig. 2 is a bottom view of the flexural plate wave sensor in accordance with the present invention;

Fig. 3 is cross sectional side view of the flexural plate wave sensor in accordance with the present invention, taken along line 3-3 of Fig. 2;

5 Fig. 4 is a graph which shows the effect on the frequency within the membrane of the sensor of the present invention to an increase in the mass of the membrane in accordance with the present invention;

Fig. 5 is a graph which shows the effect of the mass of a substance on the membrane of the sensor of the present invention on the frequency present within the membrane in
10 accordance with the present invention;

Fig. 6 is a flow chart of the operation of the first embodiment of the present invention;

Fig. 7 is a block diagram of a second embodiment of the present invention;

15 Fig. 8 is a cross-sectional side view of the flexural plate wave sensor of the second embodiment of the present invention taken along line 3-3 of Fig. 2; and

Fig. 9 is a flowchart of the operation of the second embodiment of the present invention;

Fig. 10 is a block diagram of third embodiment of the present invention;

20 Fig. 11 is a flow chart of the operation of the third embodiment of the present invention;

Fig. 12 is a block diagram of the fourth embodiment of the present invention;

Fig. 13 is a graph that shows the relationship between the mass and temperature of a substance when determining the boiling point of the substance;

Fig. 14 is a graph that shows the relationship between the frequency of the sensor and the temperature of a substance when determining the boiling point of the substance;

Fig. 15 is a flowchart of the operation of the fourth embodiment of the present invention; and

5 Fig. 16 is a schematic diagram of an array of sensors in accordance with the present invention.

PREFERRED EMBODIMENT

Mass measuring system 10, shown schematically in Fig. 1, includes a flexural plate wave sensor 12 including a membrane 14, a first transducer 16 and a second transducer 18, both disposed on membrane 14. An oscillator 20 is connected to transducer 16 for driving the membrane at a reference resonant frequency. Transducer 18 receives this frequency and transmits it to a microprocessor 22 which includes a frequency detection device 24 and a mass determining device 26. An optional display 28 may be connected to the microprocessor 22 for displaying the values determined by the system 10.

15 As shown in Figs. 2 and 3, sensor 12 includes a structural layer 30 which is preferably formed from undoped silicon, a lower layer 34 which is preferably formed from boron-doped silicon and a piezoelectric layer 36 which is preferably formed from a piezoelectric material such as aluminum nitride. Sensor 12 includes a cavity 38 (shown in phantom in Fig. 2) which is etched into the upper layer 32 and structural layer 30, leaving 20 lower layer 34 exposed within the cavity. The exposed portion of lower layer 34 forms the membrane 14 of the sensor 12. Transducers 16 and 18 are preferably interdigitated transducers.

Sub A
In operation, oscillator 20 causes transducer 16 to transmit a wave at a reference

frequency in the direction of arrow 42 which wave is received by transducer 18. The wave received by transducer 18 it is transmitted to frequency detection device 24 of microprocessor 22. Generally, as long as the mass per unit area of the membrane 14 does not change, the reference frequency input by transducer 16 and received by transducer 18 5 remains constant. However, when the mass per unit area of the membrane increases or decreases, such as when a substance is deposited or removed from the membrane, a frequency shift in the wave received by the transducer 18 results.

The amount of the change in the frequency within the membrane 14 is inversely proportional to the change in the mass on the membrane 14. For example, as shown in Fig. 10 4, if the mass of the membrane 14 is at a steady state and the reference frequency is 10MHz, an increase in the mass of the membrane by an amount Δm causes the frequency in the membrane to decrease to 9.85 MHz. By knowing that the frequency of the membrane has decreased by 150 Hz, the change in the mass of the membrane can be determined. The relationship between the mass change Δm and the frequency change Δf is shown in the 15 graph of Fig. 5. The mass sensitivity, S_m , of the sensor 12, which defines the relationship between the mass and frequency changes, is determined using the following equation:

$$S_m = \frac{(\Delta f / f_{ref})}{(\Delta m / A)}, \quad (1)$$

where f_{ref} is the reference resonant frequency input to the membrane through transducer 16 and A is the area of the membrane, which in the preferred embodiment is 5.0 mm². 20 Accordingly, the mass sensitivity S_m is determined by driving the membrane 14 at a reference resonant frequency, placing a substance of a known mass, Δm , on the membrane and measuring the change Δf in the reference resonant frequency. The relationship between

changes in the mass of the membrane Δm and the resulting changes in the frequency within the membrane Δf is then plotted to obtain the line 60.

Once the mass sensitivity S_m is known for the particular sensor 12, the mass of a substance placed on the membrane 14 can be determined with the following equation:

$$\Delta m = \frac{\Delta f}{f} \cdot \frac{A}{S_m} \quad (2)$$

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Referring to the above example, if the reference frequency f_{ref} input to the membrane 14 by oscillator 20 through transducer 16 is 10 MHz and the deposition of a substance of an unknown mass Δm causes the frequency, f_{ref} , within the membrane 14 to shift to 9.85 MHz, representing a frequency change, Δf , of 150 Hz. Using Equation (2), it can be determined 10 that this frequency change Δf corresponds to a mass change Δm of $2 \times 10^{-10} \text{ g/mm}^2$, as shown in Fig. 5.

The operation of the system 10 will now be described with reference to Fig. 6. First, oscillator 20 generates a wave of a reference frequency f_{ref} which is input to transducer 16 to drive the sensor membrane 14 at this reference frequency f_{ref} , step 62. A substance is 15 then deposited on the membrane 14, step 64, which causes a shift in the reference frequency. This shifted frequency, f_s , is received by transducer 18 and input to frequency detection device 24 which measures the shifted frequency f_s , step 66. Frequency detection device 24 then detects the frequency change in the membrane between the shifted frequency and the reference frequency by subtracting the shifted frequency from the reference frequency ($\Delta f = f_{ref} - f_s$), step 68 and outputs the frequency change, Δf , to mass determining device 26 which determines the mass of the substance based on the change in the frequency Δf , step 70.

Accordingly, as oscillator 20, Fig. 1, drives the membrane 14 at the reference resonant frequency f_{ref} of 10 MHz through the transducer 16, frequency detection device 24 of microprocessor 22 receives the frequency f detected by transducer 18. When a substance of unknown mass Δm is placed on the membrane 14, causing shifted frequency, f_s of 9.85

5 MHz to be received by transducer 18, the shifted frequency f_s is input into frequency detection device 24. Frequency detection device 24 determines the change in frequency, Δf , which is 150 Hz. This value is input to mass determining device 26 which uses Equation (2), which is shown graphically in Fig. 5, to determine the mass of the substance on the membrane 14 which, as discussed above, is 40 picograms/mm². Optional display 28 may

10 then be used to display the resulting mass value.

A second embodiment of the invention is shown schematically at 100 in Fig. 7. As shown in the figure, the only difference between system 10 of Fig. 1 and system 100 of Fig. 6 is the addition of a concentration determining device 102 within microprocessor 22. In this embodiment, system 100 is used for determining the concentration of a non-volatile residue (NVR) within a volatile solution. As shown in Fig. 8, volatile solution 104, containing NVR 106 is deposited in the cavity 38 of sensor 12 of system 100. Preferably, the volume of the solution 104 is in the range of 1 to 100 microliters. Typically, within minutes, the volatile solution 104 evaporates, leaving the NVR 106 on the membrane 14 of the sensor 12. The mass of the NVR 106 can then be determined and compared to the

15 volume of the solution in concentration determining device 102 to determine the concentration of the NVR within the solution.

The operation of the system 100 will now be described with reference to Fig. 9. First, oscillator 20 drives sensor membrane 14 at the reference resonant frequency f_{ref} , step

110. The solution 104 containing NVR 106 is then deposited on the membrane 14 within the cavity 38, step 112. After the solution 106 evaporates, step 114, the shifted frequency f_s resulting from the mass of the NVR 106 on the membrane 14 is measured, step 116. The change in frequency between the reference resonant frequency and the shifted frequency, 5 Δf , is then determined by frequency determining device 24, step 118. Mass determining device 26 then determines the mass of the NVR 106 based on the change in frequency, Δf , step 120 and the mass of the NVR 106 is compared to the volume of the solution 104 in concentration determining device 102 to determine the concentration of the NVR 106 in the solution 104. The resulting concentration measurement can then be displayed by optional 10 display 28.

The deposition of the solution 104 on the membrane 14, step 112 in Fig. 6 can be carried out in a number of ways. First, the solution can be directly deposited on the membrane by means of a microliter dropper. Alternatively, the sensor 12 could be placed in an atmosphere in which the solution 104 is present in a fluid or gaseous form, such that the 15 solution will collect on the membrane. For example, in order to test the concentration of paint particles in the atmosphere of an automotive painting facility in which paint is sprayed, the sensor 12 is placed within the facility. As the paint vapor fills the facility, a sample of the vapor will collect on the membrane. The system 100 can then be used to determine the concentration of non-volatile paint particles in the atmosphere of the facility.

20 Furthermore, the sensor can be used as a passive particle detector. In this case, the sensor is placed in an environment such as a microprocessor fabrication clean room. Since this environment must be sterile for the proper fabrication of the microprocessors, it is important to detect the presence of any foreign particles in the environment. The sensor 12

can be used to detect such particles as they contact the membrane 14 of the sensor 12.

A third embodiment of the present invention, shown schematically at 200 in Fig. 10, can be used for thermogravimetric analysis of substances, in order to determine the moisture content of a substance and the boiling point of a substance. System 200, in 5 addition to the elements shown in Fig. 1, includes a heater 202 for heating the sensor 12 for evaporating any moisture in the substance which is placed on membrane 14 of sensor 12 and a moisture content determining device 204 located within microprocessor 22.

The operation of the system 200 will now be described with reference to Fig. 11.

First, oscillator 20 drives its membrane 14 at the reference resonant frequency, f_{ref} , step 210.

10 The substance is deposited on the membrane 14, step 212, and the first shifted frequency, f_1 , resulting from the increase in mass on the membrane is determined, step 214. The frequency detection device 24 then determines the primary frequency change, Δf_p , in the membrane 14 by subtracting the first shifted frequency f_1 from the reference resonant frequency f_{ref} , step 216. Mass determining device 26 then determines the intermediate mass, 15 m_i , of the substance based on the primary frequency change Δf_p , step 218. The substance is then heated using heater 202 to evaporate any moisture in the substance, step 220. While the substance is being heated, frequency detection device 24 monitors the first shifted frequency f_1 until it becomes constant at a second shifted frequency f_2 , step 222 which occurs when all moisture has evaporated from the substance and the mass remains constant.

20 Frequency detection device 24 then determines a secondary frequency change Δf_s in the membrane 14 by subtracting the second shifted frequency f_2 from the first shift frequency f_1 , step 224. Mass determining device 26 then determines the terminal mass, m_t , of the substance based on the secondary frequency change Δf_s , step 226. Mass determining device

26 then determines the mass change Δm of the substance by subtracting the terminal mass m_t from the intermediate mass m_i , step 228, and moisture content determining device 204 determines the moisture content, M , of the substance by dividing the mass change Δm by the intermediate mass m_i , step 230.

5 Alternatively, the present invention can be used to determine the boiling point of a substance. In this embodiment, shown at 300 in Fig. 12, microprocessor 22 includes a boiling point determining device 302 in addition to the frequency determining device 24 and the mass determining device 26.

As shown in Fig. 13, as a substance is subjected to a constantly increasing 10 temperature T , the mass of the substance decreases at a steady rate as shown by line 304a until it reaches the boiling point of a substance at point 305a. Once the substance reaches its boiling point, it begins to lose mass at a greater rate, as indicated by line 306a. As discussed above, the rate of change of the mass is inversely proportional to the rate of 15 change of the frequency within the membrane 14. Accordingly, as shown in Fig. 14, as the substance loses mass as it is heated, the frequency within the membrane increases at a steady rate as shown by line 304b until the substance reaches its boiling point at the point 305b. After the substance reaches its boiling point, due to the rapid decrease in the mass of 20 the substance, the frequency within the membrane 14 increases at a greater rate, as indicated by line 306b. In the system 300 of Fig. 12, the rate of change of the frequency within membrane is monitored in order to detect the point where the rate of change of frequency of the membrane 14 changes from the constant shown at line 304b to the constant shown by line 306b, which is greater than the constant shown by line 304b.

The operation of system 300 will now be discussed with reference to Fig. 15. First,

oscillator 20 drives the sensor membrane 14 at a reference resonant frequency, f_{ref} , step 310.

The substance is deposited on the membrane 14, step 312 and it is heated by heater 202

with a temperature T which is increasing at a known rate ΔT , step 314. As the substance is

heated and begins to lose mass, frequency detection device 24 monitors the ratio of the

- 5 change in the frequency Δf in the membrane 14 which is detected by transducer 18 to the change in the temperature ΔT , step 315. If the ratio of Δf versus ΔT ($\Delta f / \Delta T$) is less than or equal to C, which represents the slope of line 304b of Fig. 14, step 316, the boiling point 305b has not yet been reached and the system continues to monitor the ratio of the frequency change to the temperature change, step 315. If the ratio $\Delta f / \Delta T$ is detected as
- 10 being greater than C, indicating that boiling point 305a, has been reached, and the frequency is now increasing at a faster rate than before the boiling point was reached, step 316. The temperature T is then recorded as the boiling point of the substance, step 318.

The sensor of the present invention also may be configured in an array as shown at 400 in Fig. 16. Array 400 includes a plurality of sensors 12 disposed on a single chip 402.

- 15 Each of the sensors 12 is connected between the oscillator 20 which inputs the reference resonant frequency to each of the sensors 12 and the frequency detection device 24 which detects a frequency change in each of the sensors 12. In the case of, for example, the paint facility or clean room environment, the frequency change in each of the sensors 12 can be averaged in order to obtain a more precise measurement of the mass change in the
- 20 environment detected by the array.

It can therefore be seen that the present invention provides an apparatus for measuring the mass of a substance by monitoring the frequency change in a membrane of a flexural plate wave sensor caused by the change in the mass of the membrane. The mass

change is determined based on the amount of the resulting frequency change. The sensitivity of the apparatus is dictated by the ability of the frequency determining device to measure the frequency change in the membrane of the sensor. Accordingly, a frequency determining device that is capable of measuring frequency changes in the single Hertz range would render the apparatus of the present invention capable of measuring mass changes in the subnanogram range.

Although specific features of the invention are shown in some drawings and not in others, this is for convenience only as each feature may be combined with any or all of the other features in accordance with the invention.

10 Other embodiments will occur to those skilled in the art and are within the
following claims:

What is claimed is: